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2,3,7-TRIMETHCXY-8,9-METHYLENEDIOXYPAVINAN – A NEW ALKALOID FROM Thalictrum strictum. II

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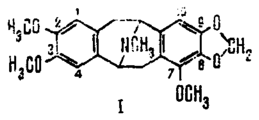
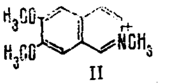
From the epigeal part of Th. strictum we have isolated a new unidentified base B (I). The alkaloid (I) is readily soluble in methanol, ethanol, and acetone and when the solvents are evaporated it separates out in the form of a faint yellowish oil. After chromatography twice on a column of alumina and concentration of the ethereal eluate, compound (I) crystallized in the form of transparent prisms with mp 144-145°C, $[\alpha]^{22}_D$ −174° (c 0.977; methanol).

UV spectrum: $\lambda_{max}^{ethanol}$ 287 nm (log ε 3.84). The NMR spectrum ($CDCl_3$, δ values, ppm) showed signals at 2.46 (singlet, 3H, NCH_3), 3.80 (singlet, 6H, $2OCH_3$), and 3.72 (singlet, 3H, OCH_3), and two one-proton doublets at 5.75 and 5.80 (J = 1.5 Hz) due to the protons of a methylenedioxy group. In the region of aromatic protons there are three one-proton singlets at 6.23, 6.36, and 6.54 ppm. Furthermore, in the 4.05-2.40 ppm region are observed signals from methine and methylene protons (6H) with characteristic splitting analogous to the corresponding protons of argemonine. The most valuable information on the structure (I) is given by its mass spectrum in which, in addition to peaks with m/e 369 M^+, 368 $(M-1)^+$, and 354 $(M-15)^+$, there are strong peaks of ions with m/e 204 (100%, II) and 218 (70%, III). The combination of the results of UV, NMR, and mass spectroscopy shows that (I) is a pentasubstituted pavinan. Since the three aromatic protons appear in the form of singlets and in the mass spectrum the main peak is that of the ion (II), the two methoxy groups must be located as in argemonine [2]. According to the biogenetic hypothesis, from one and the same benzylisoquinoline with the appropriate intramolecular cyclization both pavine and aporphine bases can be formed [3]. From the epigeal part of Th. strictum, in addition to (I) we isolated the aporphine alkaloids thalicmine, northalicmine, and thalicminine [1]. This permits the assumption that all these compounds are based on the same precursor. From the facts given, we propose for (I) as the most probable structure 2,3,7-trimethoxy-8,9-methylenedioxy-N-methylpavinan (I):


I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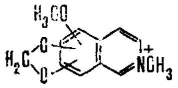
III

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